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Colorimetric and fluorimetric detection of Cu^{2+} ions in aqueous solution using styrylpyridinium dye bearing iminodiacetate receptor group

Pavel A. Panchenko, Mariya A. Ustimova, Stanislav P. Kumanev and Olga A. Fedorova

CONTENTS

1. Experimental part

Reactions were monitored by thin layer chromatography (TLC) with silica gel (DC-Alufolien Kieselgel 60 F254, Merck). Flash chromatography was performed using a Biotage IsoleraTM Prime system. Melting point was measured on Melt-temp melting point electrothermal apparatus and were uncorrected.

^{1}H and ^{13}C NMR spectra were recorded on an Avance 400 spectrometer (Bruker). The measurements were performed in DMSO-d_6 solution. The chemical shifts (given as δ) were determined with an accuracy of 0.01 ppm relative to the signals corresponding to the residual solvents and recalculated to the internal standard (TMS); the spin-spin coupling constants (J) were measured with an accuracy of 0.1 Hz. The assignment of ^{1}H and ^{13}C signals is based on 2D NMR experiments (HMBC, HSQC, ^{1}H COSY), which were performed using standard pulse sequences from the Bruker library. Numbering of carbon atoms in the compound **1** used for the description of its NMR spectra is shown in Scheme S1. ^{1}H and ^{13}C spectra of 1 are prented in Fig.S3 and S4.

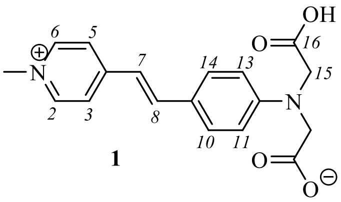
LC-ESI-MS analyses were performed using acetonitrile solutions on a Shimadzu LCMS-2020 liquid chromatography mass spectrometer.

The absorption spectra were taken on a Cary 300 spectrophotometer (Agilent Technologies). The fluorescence quantum yield measurements were performed using a Fluorolog3-221 spectrofluorimeter (Horiba Jobin Yvon). Spectral measurements were carried out in air-saturated solutions at ambient temperature. All measured fluorescence spectra were corrected for the nonuniformity of detector spectral sensitivity. Coumarin 6 in ethanol ($\varphi^{fl} = 0.78$)[S1] was used as reference for the fluorescence quantum yield measurements. The fluorescence quantum yields were calculated by the Eq. (S1),[S2]

$$\varphi^{\mathrm{fl}} = \varphi_{\mathrm{R}}^{\mathrm{fl}} \frac{S}{S_{\mathrm{R}}} \cdot \frac{(1 - 10^{-A_{\mathrm{R}}})n^2}{(1 - 10^{-A})n_{\mathrm{R}}^2} \qquad \text{(S1)}$$

wherein φ^{fl} and $\varphi_{\mathrm{R}}^{\mathrm{fl}}$ are the fluorescence quantum yields of the studied solution and the standard compound respectively; A and A_{R} are the absorptions of the studied solution and the standard respectively; S and S_{R} are the areas underneath the curves of the fluorescence spectra of the studied solution and the standard respectively; and n and n_{R} are the refraction indices of the solvents for the substance under study and the standard compound.

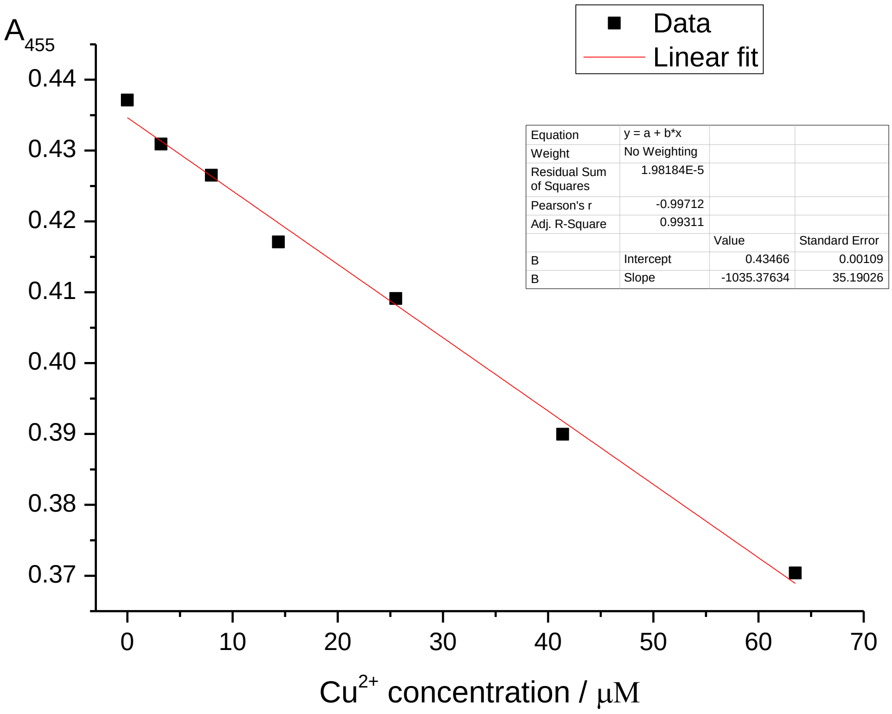
Complex formation of compound **1** with Cu^{2+} was studied by spectrofluorometric and spectrophotometric titration.[S3,S4] The ratio of **1** to Cu^{2+} was varied by adding aliquots of a solution of copper(II) perchlorate in water of known concentration to a solution of ligand **1** in the acetate buffer (0.1 M, pH = 5.9). The fluorescence or absorption spectrum of each solution was recorded, and the stability constants of the complexes were determined using the SPECFIT/32 program (Spectrum Software Associates, West Marlborough, MA).



1

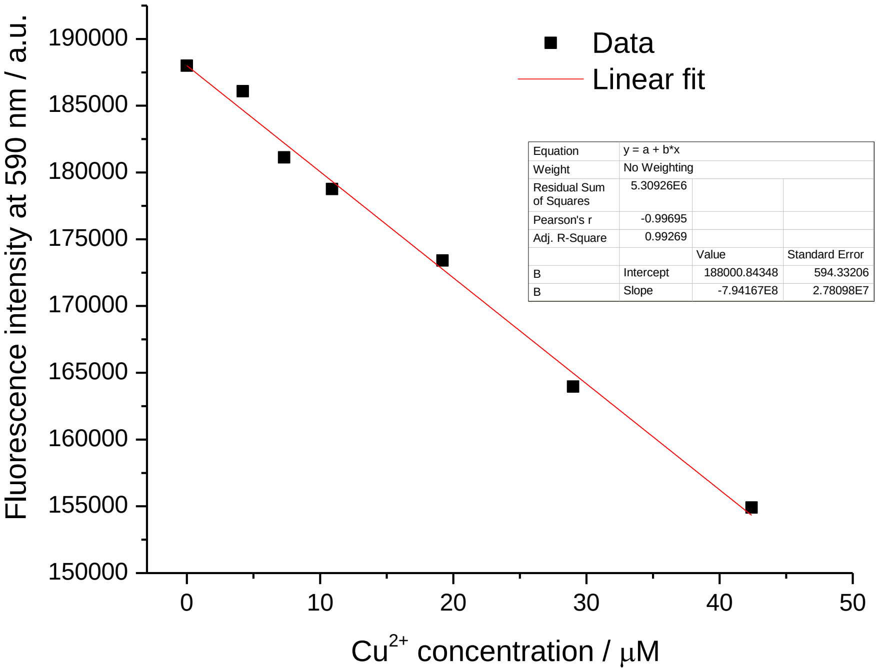
Compound **1**. A solution of 2,2′-(4-formylphenylazanediyl)diacetic acid **5** (0.1 g, 0.42 mmol), 1,4-dimethylpyridinium iodide **6** (0.08 g, 0.34 mmol), piperidine (51 μl, 0.51 mmol) in abs. ethanol (3 ml) was boiled under microwave irradiation for 3 hours. Then the reaction mixture was cooled and the resulting precipitate was filtered, washed with hexane, ethyl acetate and diethyl ether and dried. Red solid, yield 56% (0.063 g). ^{1}H NMR (400.13 MHz, DMSO-d_6, 20°C, δ / ppm, J / Hz): 4.05 (s, 4H, H(15)); 4.16 (s, 3H, $N^+(CH_3)$); 6.53 (d, 2H, H(11), H(13), J = 8.9); 7.17 (d, 1H, H(7), J_{trans} = 16.0); 7.58 (d, 2H, H(10), H(14), J = 8.9); 7.89 (d, 1H, H(8), J_{trans} = 16.0); 8.05 (d, 2H, H(3), H(5), J = 6.2); 8.67 (d, 2H, H(2), H(6), J = 6.2). ^{13}C NMR (150.93 MHz, DMCO-d_6, 25°C, δ / ppm): 46.4 ($N^+(CH_3)$); 57.3 (C(15)); 111.4 (C(11), C(13)); 117.7 (C(7)); 122.3 (C(3), C(5)); 123.3 (C(9)); 130.1 (C(10), C(14)); 141.7 (C(8)); 144.4 (C(2), C(6)); 149.4 (C(12)); 153.3 (C(4)); 173.2 (C(16)). ESI-MS in MeOH, m/z: found, 327.00; calculated, 327.13 ($[M+H]^+$). Found (%): C, 64.32; H, 5.64; N, 8.33; I, 0.75. $C_{18}H_{18}N_2O_4 \cdot 0.02HI \cdot 0.4H_2O$. Calculated (%): C, 64.44; H, 5.85; N, 8.12; I, 0.7.

2. Figures S1–S5



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.98184E-5		
Pearson's r	-0.99712		
Adj. R-Square	0.99311		
		Value	Standard Error
B	Intercept	0.43466	0.00109
B	Slope	-1035.37634	35.19026

Figure S1. Plot of the absorption at 455 nmfor sensor **1** (12.5 μM) *versus* increasing concentrations of copper(II) perchlorate in the solution. Solvent – aqueous acetate buffer (0.1 M, pH 5.9).



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	5.30926E6		
Pearson's r	-0.99695		
Adj. R-Square	0.99269		
		Value	Standard Error
B	Intercept	188000.84348	594.33206
B	Slope	-7.94167E8	2.78098E7

Figure S2. Plot of the fluorescence intensity at 590 nm for sensor **1** (12.5 μM) *versus* increasing concentrations of copper (II) perchlorate in the solution. Excitation wavelength is 369 nm. Solvent – aqueous acetate buffer (0.1 M, pH 5.9).

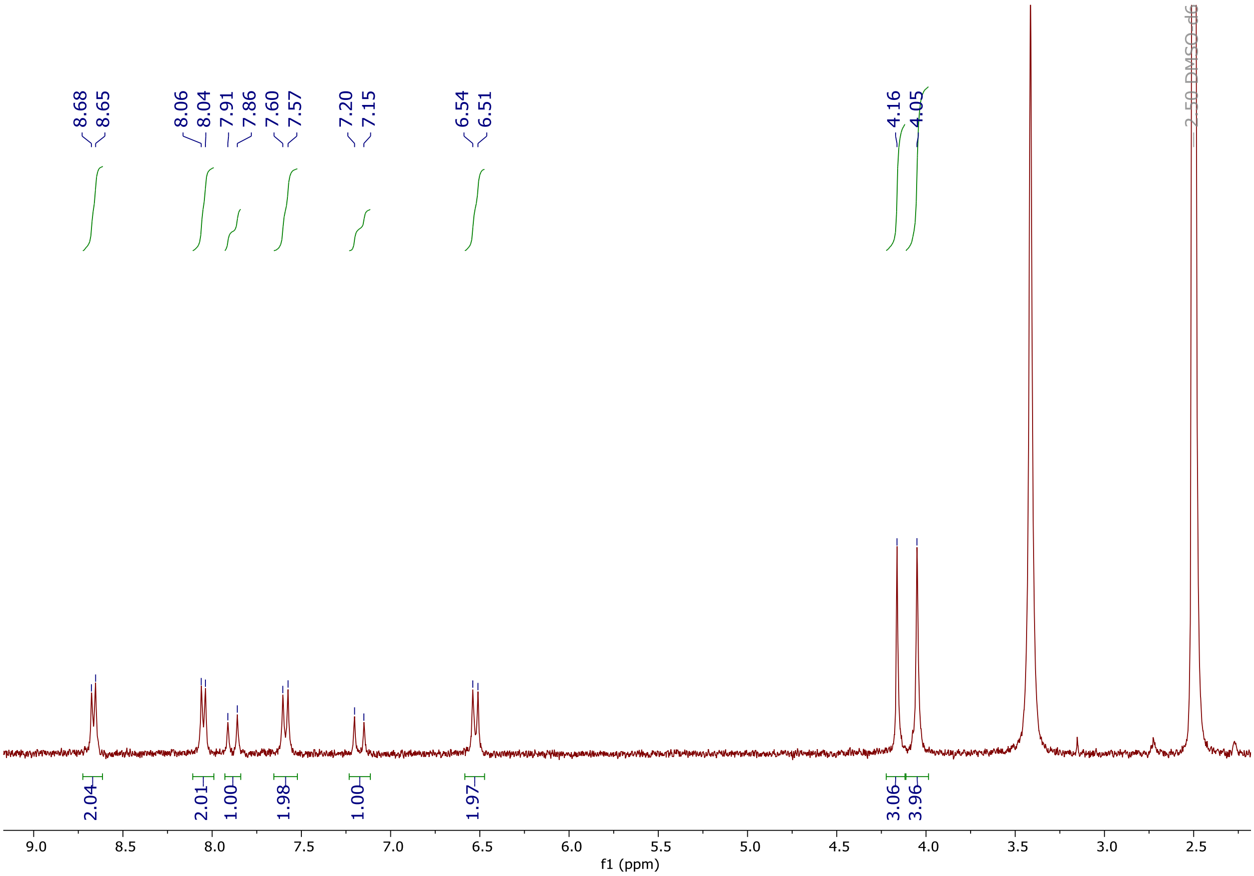


Figure S3. ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

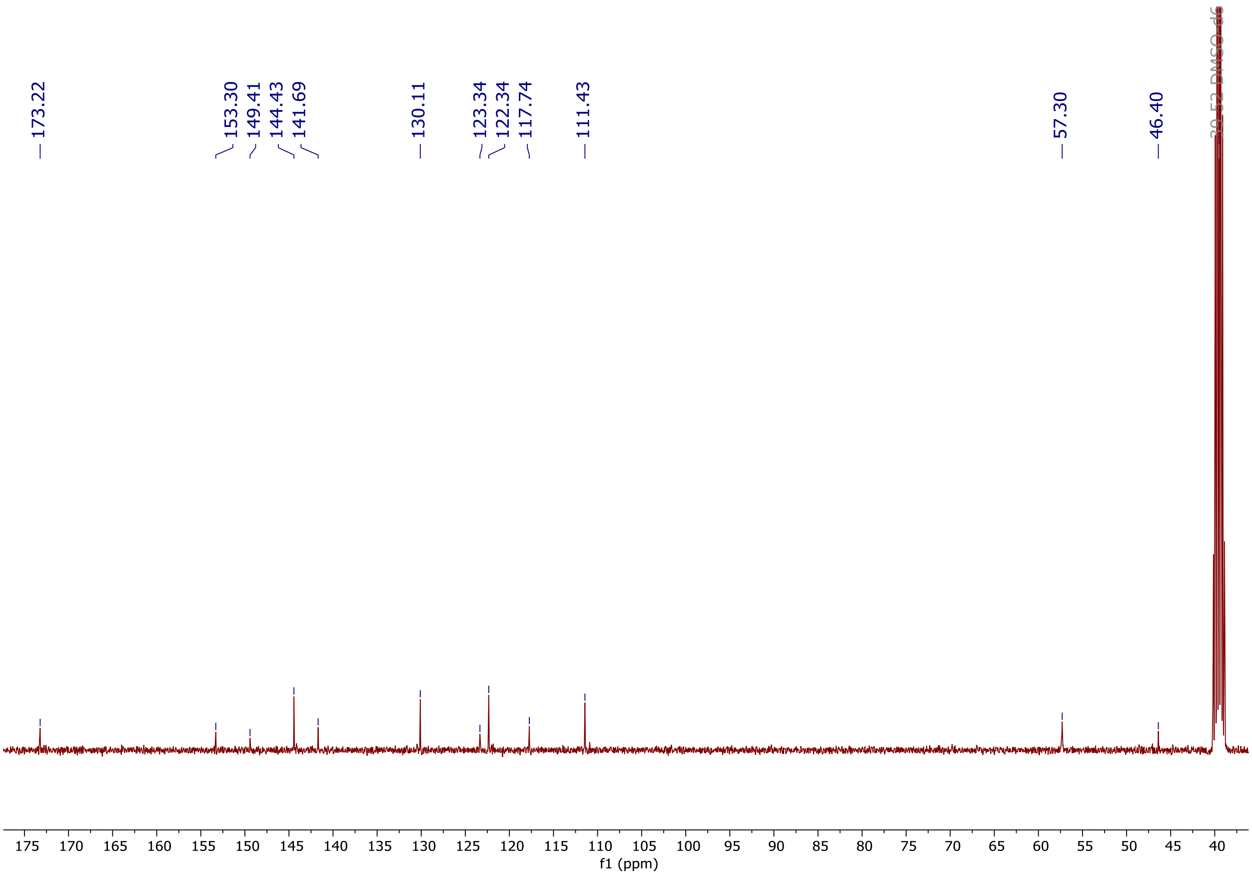


Figure S4. ^{13}C NMR spectrum of compound **1** in DMSO-d_6.

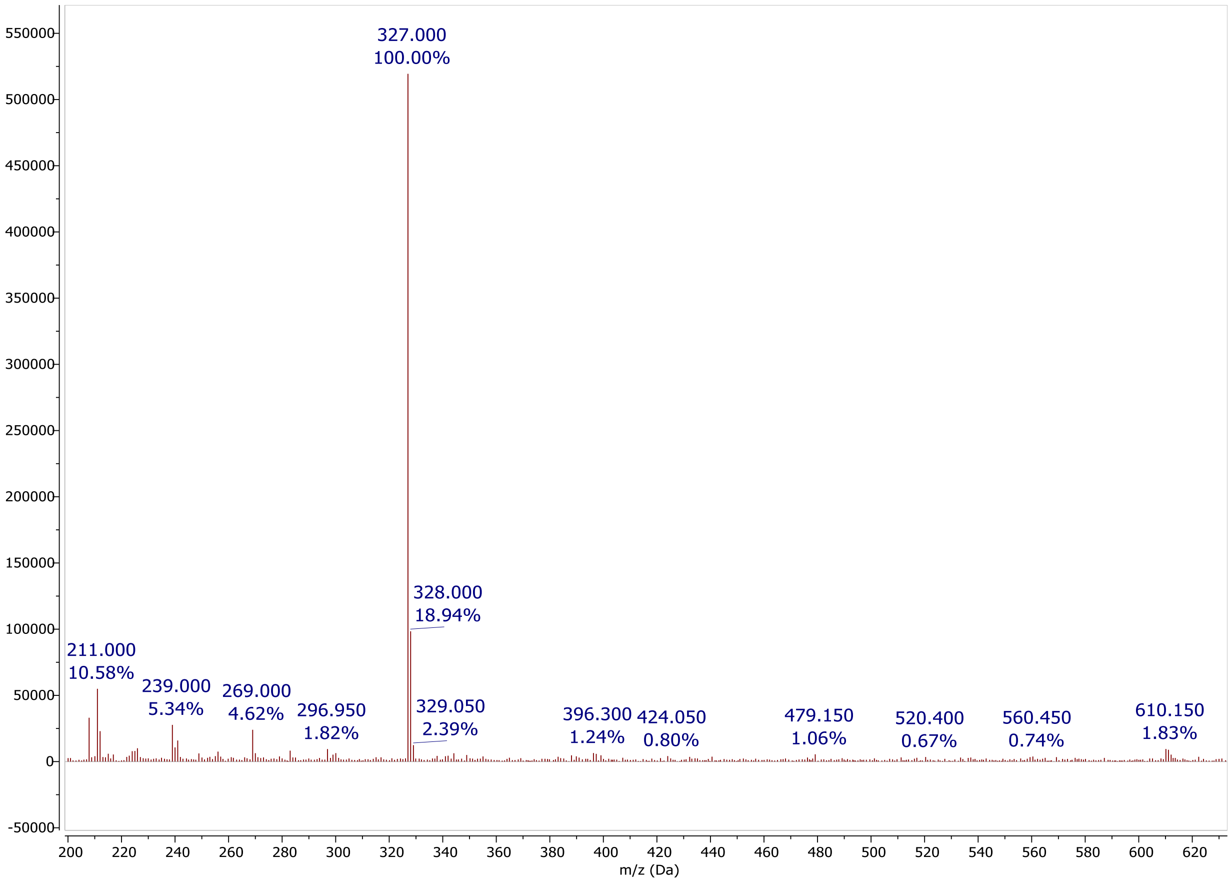


Figure S5. HR-ESI-Mass spectrum of compound **1**.

3. References

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